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DAY OF THE WEEK VARIATIONS OF PHOTOCHEMICAL POLLUTANTS IN THE ST. LOUIS AREA

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Abstract – As part of the Environmental Protection Agency's Regional Air Pollution Study (RAPS) a network of 25 stations continuously recorded aeromatic data in the Greater St. Louis area. Various photochemical pollutants (O_3, NO, NO_2 and total hydrocarbons) and some selected meteorological variables (wind speed, temperature, and solar radiation) were analyzed with respect to the day of the week using 11 months of data collected during the warm months of the year – periods during which high ozone concentrations were common in St. Louis. The results reveal that the sign (±) of the workday to Sunday differences in the concentration of ozone depends to a large extent on the distance of the measurement from the major emission area of the metropolitan area of St. Louis. The data suggest that this is due to the impact of nitric oxide on the ambient ozone concentrations. This appears to offer at least a partial explanation for some of the contrasting results reported by various investigators regarding the differences in ozone concentrations between weekends and weekdays.

INTRODUCTION

In recent years, apparently conflicting results have been reported regarding the behavior of ozone on workdays vs Sundays. Cleveland *et al.* (1974) have shown, in a detailed statistical analysis, higher ozone concentrations on Sundays as opposed to workdays (Monday–Friday) for two stations located in areas of high emissions of primary pollutants. These results are in contrast to the difference in weekend vs weekday oxidant concentrations measured at Pasadena, California by Schuck *et al.* (1965). They reported lower oxidant concentrations on weekends as opposed to weekdays. Bruntz *et al.* (1974) investigated a number of stations in New Jersey and New York and found little difference in the diurnal pattern of ozone on weekends as opposed to weekdays. The California Air Research Board (1974) reported a progressive increase in ozone concentrations from Monday to Friday with a pronounced decrease in the concentrations on weekends for three stations located in the northeast portion of the Los Angeles Basin. Recently an analysis by Elkus and Wilson (1977) revealed lower ozone concentrations during the summer on Sundays for some inland stations in the Los Angeles Basin and the opposite effect for stations located closer to the coast.

The daily emissions and motor vehicle traffic patterns on workdays (Monday–Friday) change on Saturdays and Sundays. If ozone concentrations are to be reduced below certain undesirable levels it is important to fully explore the effect these variations have on ambient ozone concentrations. Data collected by the Environmental Protection Agency in the Regional Air Pollution Study (RAPS) in St. Louis, Missouri provide the opportunity to examine day-of-the-week variations of photochemical pollutants in a comprehensive manner.

PROCEDURES

Figure 1 depicts the locations of the 25 Regional Air Monitoring System (RAMS) sites in St. Louis and vicinity. Each site was categorized as inner, transitional, or outer based on: (1) the ambient concentrations of photochemical pollutants at these sites, (2) the distance of the sites from downtown St. Louis, and (3) the emission pattern of the primary photochemical pollutants, total hydrocarbons and the nitric oxides (NO_x) in the St. Louis area. Stations 101–107 were grouped together to form the inner sites, the transitional sites consisted of stations 108–120, and stations 121–125 formed the outer sites. Ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), total hydrocarbons (THC), surface temperature, and wind speed were recorded at all 25 RAMS sites. Pyranometers, used to measure the total incident solar radiation, operated at sites 103, 104, 108, 114, 118, and 122. The intake height for the photochemical pollutants was 4 m above the ground. The temperature was measured at 5 m above the surface while the wind speed was recorded atop 10- or 30-m towers.

For the three groups of sites, 24-h averages as well as 16-h averages of all the variables, except the total incident solar radiation, were calculated every day from July to October, 1975 and April to October, 1976.

* On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

Fig. 1. The regional air monitoring stations in St. Louis.

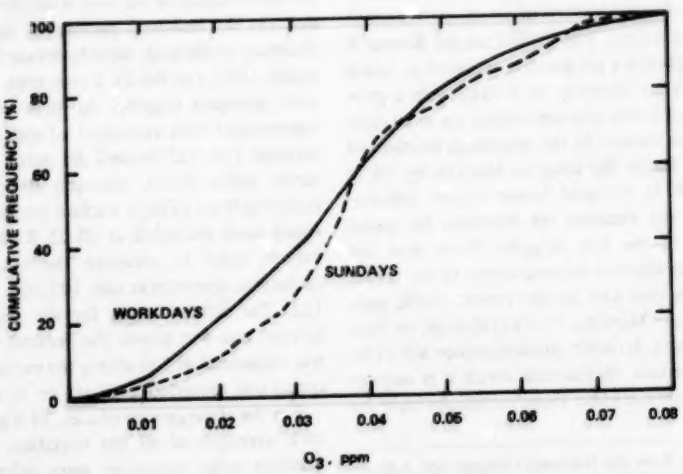

Fig. 2. Ogives for 16-h average O_3 concentrations on Sundays and workdays for the inner sites.

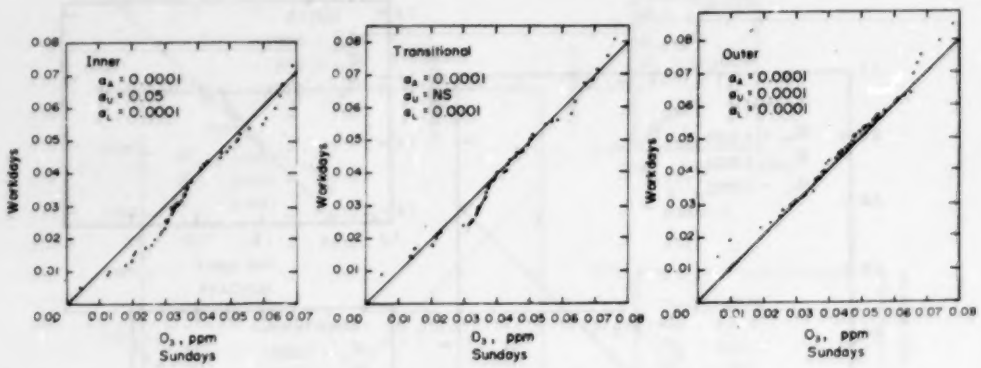

Fig. 3. Quantile–quantile plots of ozone for Sundays vs workdays. α gives the significance level for rejection of the null hypothesis that there is no difference between paired values. Subscript A denotes all quantiles plotted; U denotes quantiles at or above the 50th percentile; L denotes quantiles at or below the 50th percentile. NS implies no significance, the null hypothesis must be accepted.

For the incident solar radiation, the daily total was calculated. The 16-h averages were calculated during the interval between 0600 Central Standard Time (CST) and 2200 CST. Two averaging periods were chosen for analysis because peak concentrations of all the photochemical pollutants do not occur during the same time of day.

As part of the day-to-day (Monday vs Tuesday, Tuesday vs Wednesday... Saturday vs Sunday and Sunday vs Monday) and workday (Monday inclusively to Friday) to Sunday comparisons of the photochemical pollutants and the meteorological variables a statistical technique known as a quantile–quantile (Q–Q) plot (Wilk and Gnanadesikan, 1968) was employed. The construction of a Q–Q plot can proceed directly from two ogives such as those depicted in Fig. 2. The Q–Q plot for the data sets represented in Fig. 2 simply consists of plotting the O_3 averages on Sundays vs workdays for identical quantiles as given by the ordinate values for the ogives. Fig. 3 contains the Q–Q plot based on the ogives shown in Fig. 2. If the Sunday vs workday averages were identically distributed, then the plot of Sunday-quantiles vs workday-quantiles would have fallen along a straight line with a slope equal to one. The number of quantiles plotted in the Q–Q plots matched the number of observations in the smallest data set (the Sunday data set in this paper).

The Q–Q plots are an exceptionally useful tool in detecting distributional differences in data sets. Furthermore, Q–Q plots do not require any assumption regarding the distribution of the values within the data sets and the statistical significance of the Q–Q plots can be assessed by non-parametric tests. The Wilcoxon matched-pair signed-rank test was used to test the null hypothesis that there was no difference between the Sunday- vs workday-quantiles plotted in the Q–Q plots (See Panofsky and Brier, 1968 or Siegel, 1956 for a description of the Wilcoxon test). These characteristics make this technique ideally suited for day-of-the-week aerometric data analysis.

In addition to the Q–Q plots, diurnal curves based on hour averages were computed for all the photochemical variables on workdays, Sundays, and all days regardless of the day of the week. These curves were formed for the three groups of sites. During the 11 months of study the diurnal curves were computed on a monthly basis as well as averaged over the entire period of study.

RESULTS

The Q–Q plots of 16-h average concentrations of O_3, THC, NO_2, and NO are presented in Figs 3–6 for Sunday vs workday comparisons. In Fig. 3 the O_3 averages for the outer sites are lower on Sundays as opposed to workdays for nearly all quantiles, but the O_3 averages for the inner sites depict an increase in concentration on Sundays vs workdays, attributable to higher concentrations at low and high quantiles. When considering all quantiles the transitional sites also had significantly higher O_3 averages on Sundays as opposed to workdays, but this is mainly attributable to higher concentrations at low quantiles. For THC the Q–Q plots (Fig. 4) reveal that for all three groups the averages were less on Sundays, but the difference between the Sunday and workday averages was larger and more significant for the sites nearest to the inner group. Since the naturally-occurring portion of the THC measurement, including methane, arises from biological sources and can thus be considered more or less constant, much of the decrease in the THC concentrations on Sundays can be attributed to a

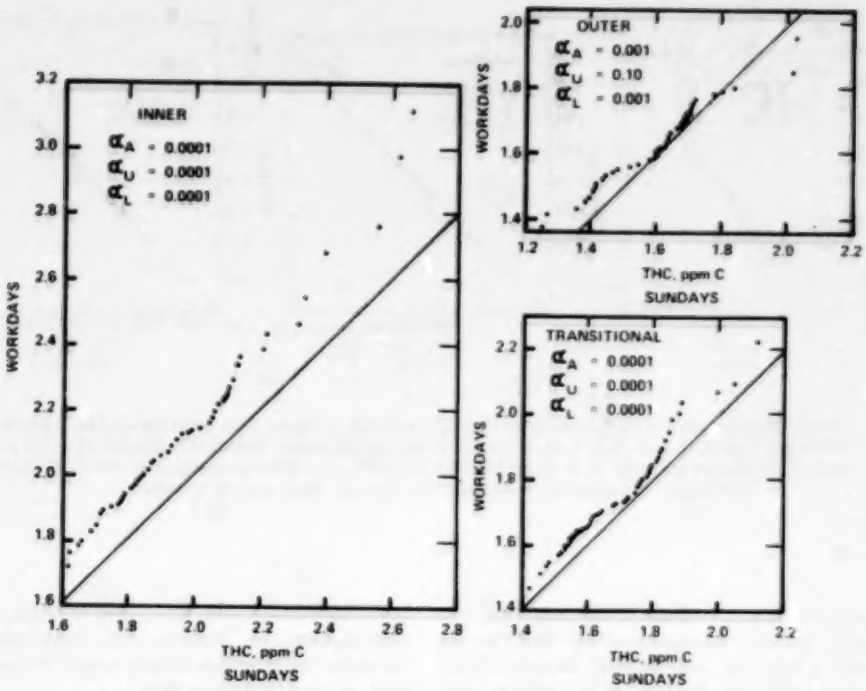

Fig. 4. Quantile–quantile plots of total hydrocarbons for Sundays vs workdays.

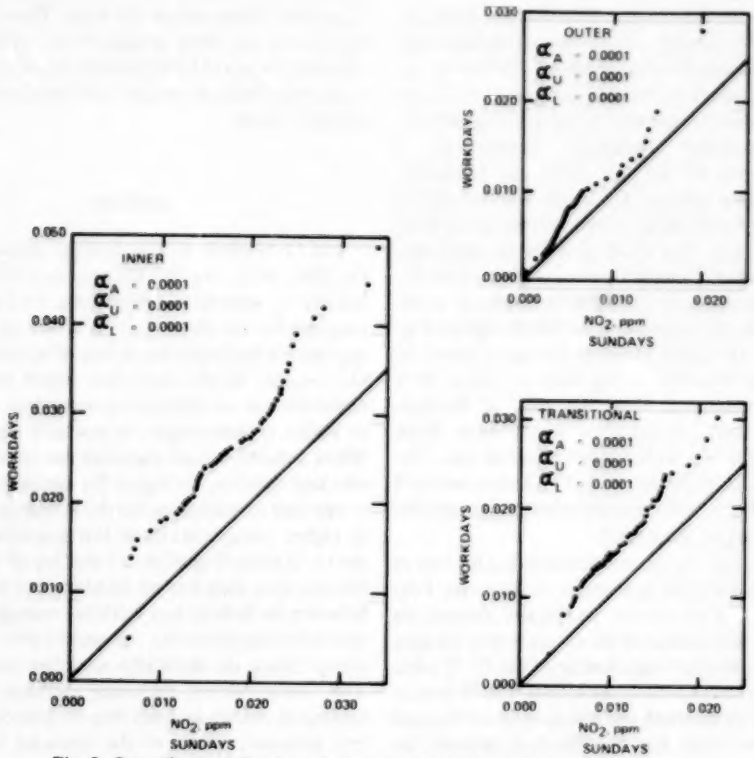

Fig. 5. Quantile–quantile plots of nitrogen dioxide for Sundays vs workdays.

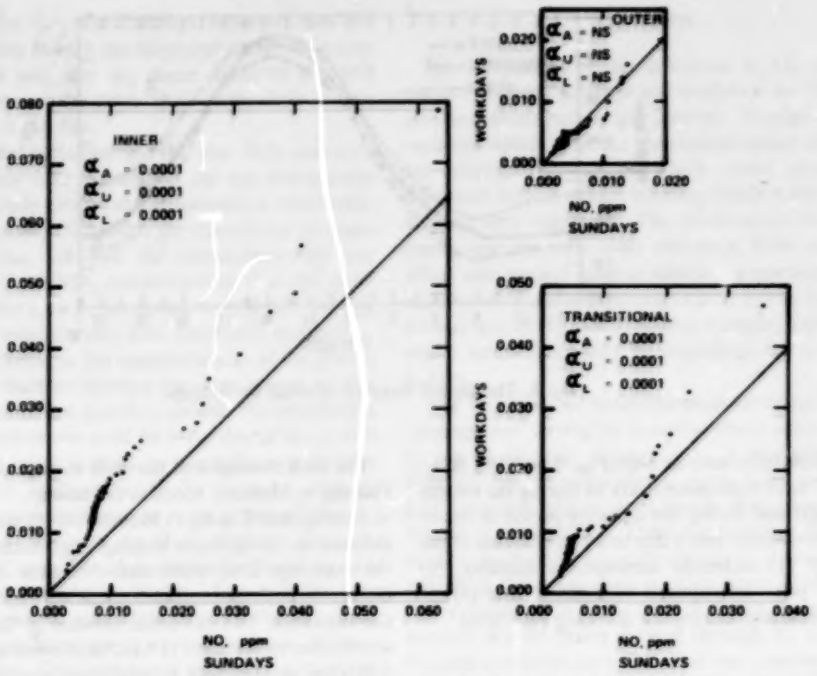

Fig. 6. Quantile–quantile plots of nitric oxide for Sundays vs workdays.

decrease in nonmethane hydrocarbons (NMHC).* The NO_2 Q–Q plots depict a decrease in NO_2 averages on Sundays for all three groups and for all quantiles with the largest decreases occurring at the inner sites (Fig. 5). For the pollutant NO care must be exercised when interpreting the Q–Q plots particularly at the outer sites. At the inner sites NO averages are lower on Sundays than on workdays at all quantiles, but at the transitional sites, although still highly significant, the reduction of NO averages on Sundays is less pronounced. The NO averages for the outer sites are close to the lowest detectable limit of the instrument especially at low and middle quantiles for both workdays and Sundays. Therefore the change in concentration of NO averages from workdays to Sundays, in addition to being statistically insignificant, has little significance for these outer sites.

The 24-h workday vs Sunday Q–Q plots are not presented because they are nearly identical to the 16-h average Q–Q plots. This similarity further substantiates the credibility of the results of the Q–Q plots since O_3 was the only pollutant which had its peak concentrations during the middle of the day (Figs 7

* Methane was also measured in RAPS. However, the measurement of NMHC, based on the subtraction of methane from THC was often unreliable. Concentrations of NMHC calculated in this manner were often below the detection level of the THC and methane measurements individually.

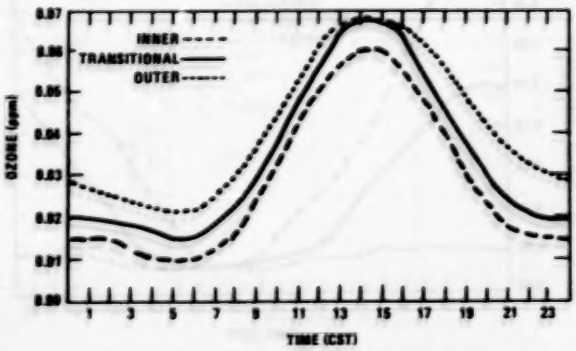

Fig. 7. The diurnal variation of ozone on workdays.

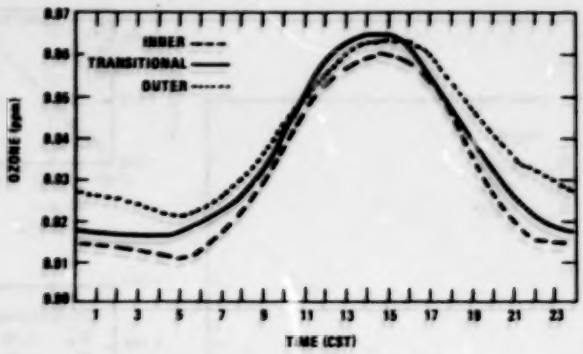

Fig. 8. The diurnal variation of ozone on Sundays.

and 8). Pollutants such as NO (Figs 9 and 10), NO_2, and THC have high concentrations during the middle of the night and during the morning period of heavy traffic. Presumably this is due to a combination of the following: (1) increased atmospheric stability, (2) relatively poor atmospheric ventilation, and (3) increased emissions during the morning rush hour.

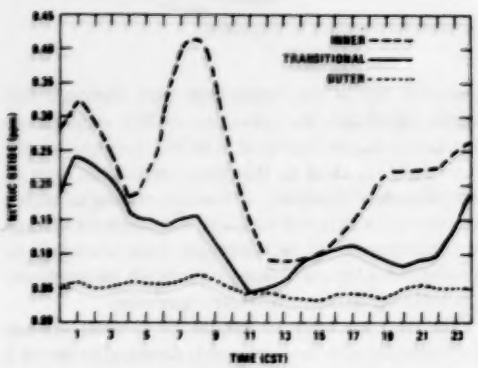

Fig. 9. The diurnal variation of nitric oxide on workdays.

The 16-h average and the 24-h average day-to-day (Sunday vs Monday, Monday vs Tuesday, ... Saturday vs Sunday, and Sunday vs Monday) Q–Q plots did not indicate any progressive buildup of pollutants during the weekdays. Only small non-systematic day-to-day changes in pollutant concentrations were noted during the weekdays. The difference between pollutant concentrations on Sundays vs Saturdays compared to the difference on Sundays vs workdays were similar in sign, but less in magnitude.

Throughout the day on workdays the outer sites averaged higher ozone concentrations than either the transitional or inner sites (Fig. 7). On Sundays however, during the middle of the day the transitional sites had the highest ozone concentrations of the three groups (Fig. 8). During the hours of peak ozone concentrations on workdays the difference between the concentrations of the inner and outer groups of sites was twice the difference between these same two groups of sites on Sundays. A similar characteristic can be found in the difference of NO concentrations between the inner and outer sites (Figs 9 and 10). The NO concentrations for the inner sites on workdays average higher than any other group of sites through-

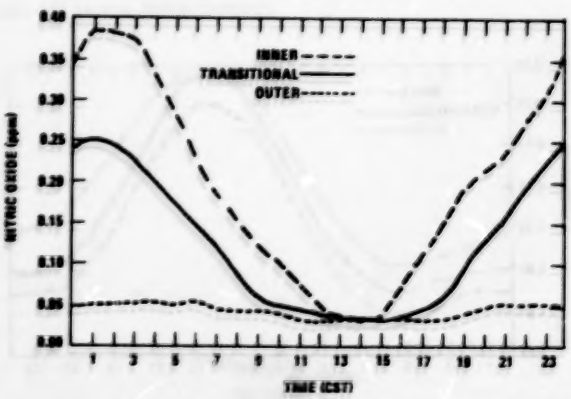

Fig. 10. The diurnal variation of nitric oxide on Sundays.

out the entire day. On Sundays however, the NO concentrations in both the inner and transitional sites are reduced and they are much closer to the NO concentrations at the outer sites, particularly during the middle of the day.

The diurnal variation of THC and NO_2 was such that the inner sites throughout the day consistently had significantly greater concentrations on both workdays and Sunday than either the transitional or outer group of sites. Likewise the transitional sites had higher THC and NO_2 concentrations than the outer sites except for a few hours during the middle of the day when the concentrations were essentially identical.

The differences in the concentrations of the photochemical pollutants between the three groups of sites were consistent from month to month. The implication that these differences hold on every day of the month would be in error. Indeed, on a specific workday for example, the highest hourly O_3 averages may be located at the transitional or inner group of sites.

Figures 11–13 depict the Q–Q plots for the 16-h average wind speed, the 16-h average temperature, and the total solar radiation. Figure 11 reveals the tendency for stronger wind speeds on Sundays as significantly greater wind speeds were observed at all three groups of sites. This tendency is most pronounced for the highest quantiles, but is also characteristic for the lower wind speeds as indicated by the Wilcoxon test. It is noteworthy that the Q–Q plots for the three groups are very similar. The Q–Q plots of temperature also depict quite similar distributions for all three groups (Fig. 12). Lower temperatures were observed on Sundays at most quantiles, being most pronounced near 15 and 25°C. All three groups receive more solar radiation on Sundays at all the quantiles except for the very low quantiles (Fig. 13).

For the three meteorological variables, wind speed, temperature, and total solar radiation the Q–Q plots were quite similar for the three groups of sites, unlike the Q–Q plots for the photochemical pollutants. No differences could be detected between the 16-h and the 24-h average Q–Q plots for the meteorological variables.

DISCUSSION

The variability of the difference in O_3 concentrations between Sundays and workdays for the three groups of sites needs further scrutiny. Weather-related variables which influence the concentration of O_3 do not display peculiarities which could cause the difference in O_3 averages between Sundays and workdays to vary regionally. The temperature, the wind speed, and the total solar radiation, three variables which can explain quite a substantial portion of the variance of the daily O_3 averages in St. Louis (Karl and DeMarrais, 1977), had Sunday to workday differences which were remarkably homogeneous for the three groups.

The fact that the meteorological variables do not "average out" during the period of study, as evidenced by the Q–Q plots (Figs 11–13), is important. On Sundays lower temperatures, more solar radiation, and somewhat higher wind speeds were observed as compared to workdays. These conditions in St. Louis tend to occur more frequently shortly (1–2 days) after a cold frontal passage than at other times. Evidence of this is contained in Table 1 which depicts an increased number of cold fronts moving through St. Louis on Fridays and Saturdays. The table was compiled using the Daily Weather Maps. Only cold fronts which appeared on the maps on both the day before and the day after their passage through St. Louis were counted. This tends to eliminate weak fronts which sometimes become stationary and shortly thereafter move back over the regions previously crossed. Others (Morgan *et al.*, 1975) have also shown that cold frontal passages are not at all uncommon in the St. Louis area even in July.

In St. Louis the days shortly after a cold frontal passage are associated with below normal daily O_3 averages (Karl and DeMarrais, 1977). On the basis of this fact the weather conditions during the period of study would favor a tendency for lower O_3 averages to be observed on Sundays as opposed to workdays. This implies that the increased O_3 concentrations observed at the inner sites on Sundays could have been even

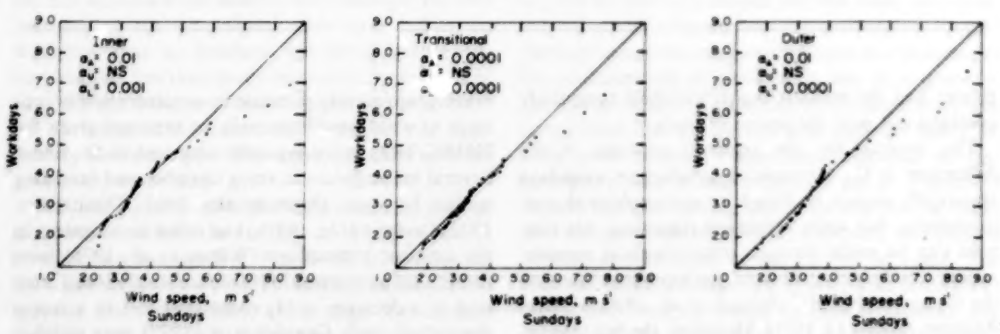

Fig. 11. Quantile–quantile plots of wind speed for Sundays vs workdays.

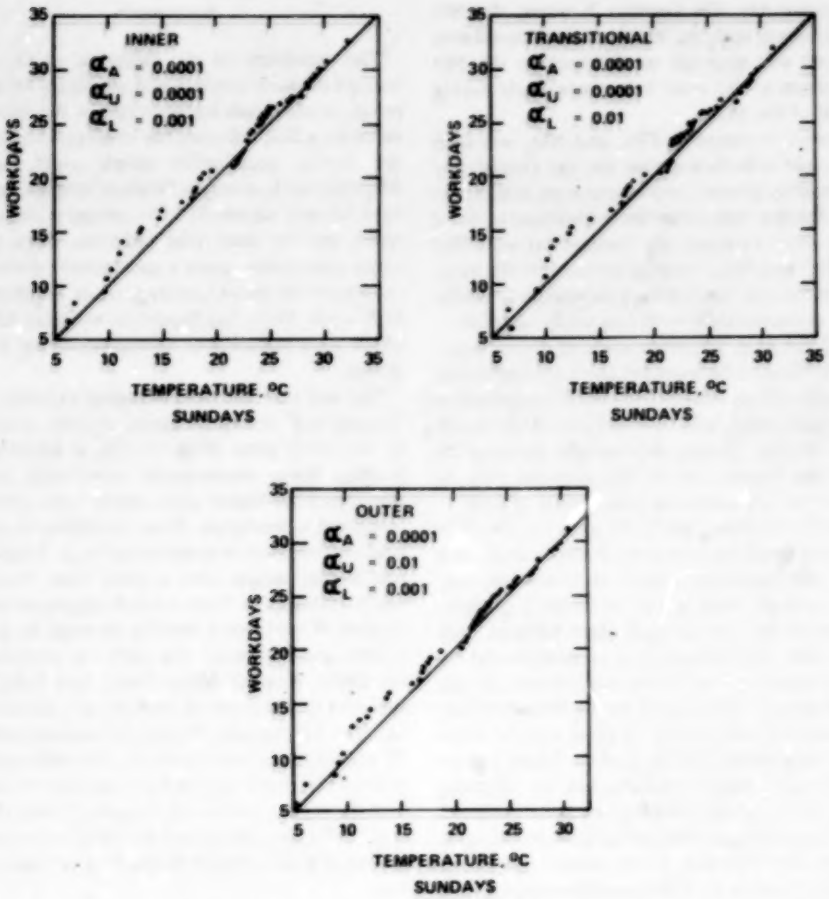

Fig. 12. Quantile–quantile plots of temperature for Sundays vs workdays.

Table 1. Cold frontal passages through St. Louis categorized with respect to the day of the week during the period of study (July–October, 1975 and April–October, 1976)

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
5	2	7	6	7	10	9

greater had the meteorological variables completely averaged out over the period of study.

The reasons for the regional contrast in the differences in O_3 averages on Sundays vs workdays apparently cannot be found by meteorological considerations, but some inferences regarding this contrast can be made through some chemical considerations. Oxidant control strategies have been based on the control of NMHC (Schuck *et al.*, 1970; Federal Register, August 14, 1971). Therefore, the fact that O_3 averages increase at the inner sites on Sunday while NMHC apparently decrease in concentration is contrary to what would normally be expected given the NMHC/NO_x ratios typically observed in St. Louis. Several investigators in smog chamber and modeling studies however, (Romanovsky, 1967; Dimitriades, 1972; Dodge 1977a, 1977b) and other investigators in the ambient atmosphere (Wilson *et al.*, 1976) have shown that an increase in NO concentrations can often lead to a decrease in O_3 concentrations. In a recent theoretical study Graedel *et al.* (1977) have satisfactorily reproduced the results reported by Bruntz *et al.*

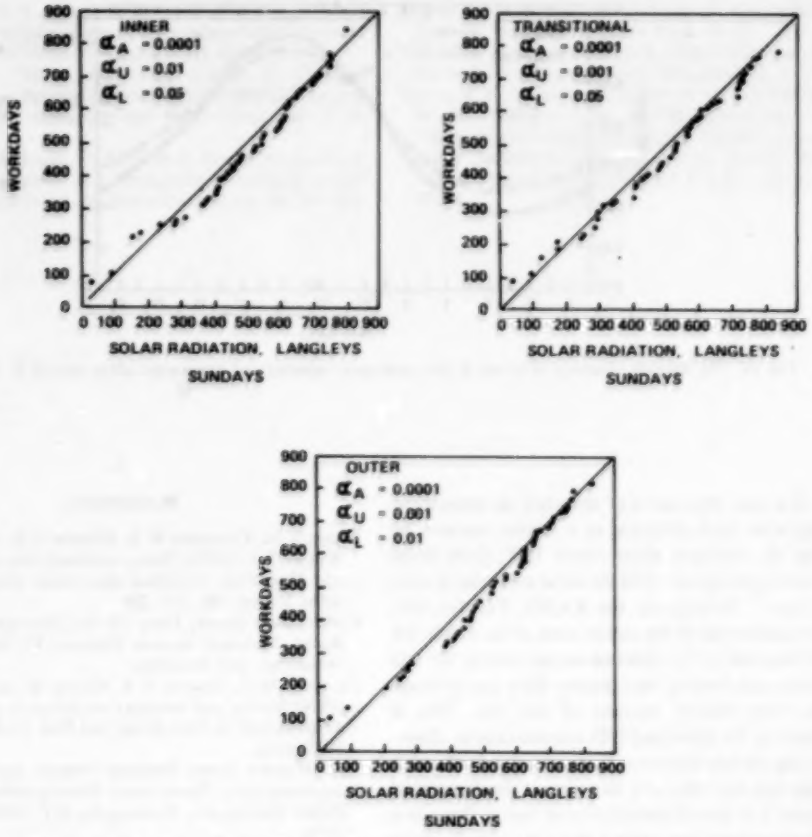

Fig. 13. Quantile–quantile plots of total solar radiation for Sundays vs workdays.

(1974). The computations by Graedel *et al.* (1977) also point out the importance of ozone scavenging by NO. In St. Louis the increase in NO averages from Sundays to workdays was most pronounced at the inner sites where the O_3 averages decreased from Sundays to workdays at both high and low quantiles (Figs 3 and 6). At the outer sites, where NO averages remain very low on Sundays as well as on workdays, O_3 averages did not decrease from Sundays to workdays. The NO averages at the transitional sites were higher on workdays than on Sundays, but the difference was considerably less than that observed at the inner sites. Fig. 3 indicates that overall the O_3 averages were lower on workdays at the transitional sites, but not significantly for both upper and lower quantiles as is the case at the inner sites.

The consequence of high NO concentrations can also be inferred from the diurnal curves of O_3 and NO on workdays and Sundays (Figs 7–10). O_3 averages at the inner sites, where NMHC concentrations are the highest, always remained lower than the concentrations at the transitional or outer groups of sites while the NO concentrations at the inner sites were consistently greater than or equal to the NO concentrations of the other groups. On Sundays the transitional sites have O_3 concentrations which surpass the outer sites during the middle of the day. At this time the NO concentrations of both groups are nearly the same.

An attempt was made to ascertain the effect NO has on the diurnal variation of O_3. In Fig. 7 the slope of the O_3 curves are very similar for the inner and transitional areas during the late afternoon and evening. At the outer group of sites, however, the rate of decrease of O_3 concentration is significantly less. It is probable that the increased NO concentrations of the inner and transitional sites during this time depleted the O_3 in these areas causing a more rapid decrease in concentration than would otherwise occur. Figure 14 depicts the average O_3 concentrations for the outer sites categorized with respect to the sites being either upwind or downwind of the City of St. Louis. The resultant wind based on hourly wind data throughout the RAMS was calculated to classify upwind and downwind sites. If the resultant wind vector with its tail centered on downtown St. Louis passed within

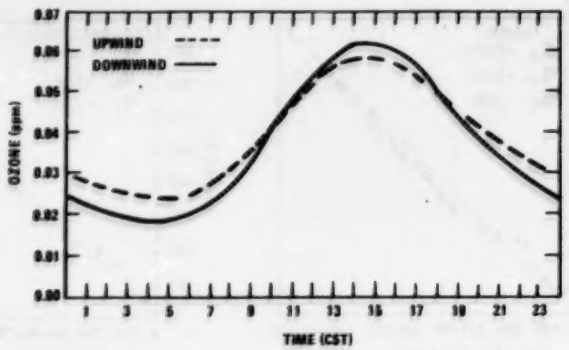

Fig. 14. The diurnal variation of ozone in the rural areas upwind and downwind of the city of St. Louis.

$\pm 45°$ of a site, that site was classified as downwind. Upwind sites were obtained in a similar manner by rotating the resultant wind vector 180°. Only those hours were considered when the wind averaged greater than $2\,m\,s^{-1}$ throughout the RAMS. For the sites located downwind of the urban area of St. Louis the rate of decrease of O_3 concentrations during the late afternoon and evening was greater than the decrease for the sites located upwind of the city. This is attributed to the increased NO concentrations observed during the late afternoon that continue on through the night and into the early morning at the downwind outer sites. It is also of interest to note that at these sites O_3 concentrations throughout the night remain lower than the concentrations at the upwind outer sites. This may also be attributed to the observed increased NO concentrations resulting from the transport of NO from the urban area.

SUMMARY

The contrasting reports from various locations regarding the differences of O_3 concentrations on the weekend vs the weekdays appear quite plausible in light of the results reported here. In St. Louis the difference in the concentrations of the photochemical pollutants NO, NO_2 NMHC, and O_3 from Sundays to workdays depended to a large extent on the distance of the measurement from the urban area of St. Louis. Concentrations of O_3 were observed to decrease from Sundays to workdays inside the city of St. Louis, in contrast to observations at stations located tens of kilometers outside the city. Meteorological conditions were not responsible for these regional differences. The data suggest that the increase from Sunday to workdays of NO concentrations inside the city was responsible for the decrease of O_3 concentrations observed on workdays inside the city.

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